Registry No. $[PEt_3AgI]_4$, 55853-47-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC50269L-10-75.

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$$\sigma(\text{of average}) = \left[\sum_{i=1}^{i=N} (\chi_i - \bar{\chi})^2/(N-1)\right]^{1/2}$$

Here χ_i is the ith value and $\bar{\chi}$ is the mean of the N values.
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Crystal and Molecular Structure of a 1:2 Cyclobutadieneiron Tricarbonyl–Dimethyl Maleate Photoadduct

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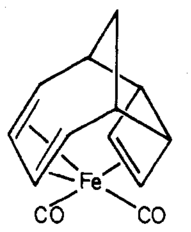
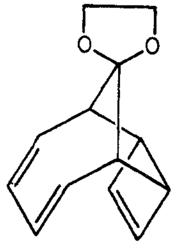
The crystal structure of $C_{16}H_{20}O_8Fe(CO)_3$, a 1:2 cyclobutadieneiron tricarbonyl–dimethyl maleate photoadduct, has been determined by single-crystal X-ray diffraction techniques using three-dimensional data gathered by counter methods. Crystals are pale yellow plates, of orthorhombic space group $P2_12_12_1$ with unit cell parameters at 23 (1)° of a = 15.646 (2), b = 23.941 (2), and c = 11.033 (1) Å. A calculated density of 1.550 g cm^{-3} for eight formula units of $C_{16}H_{20}O_8Fe(CO)_3$ per cell agrees with the measured value of 1.551 g cm^{-3}. The two discrete molecules of the asymmetric unit are related by a pseudo-b-glide plane at $x \simeq 0.26$, approximating space group *Pbca*. Each Fe atom is coordinated to a distorted octahedron of carbon atoms—three CO molecules which form a $Fe(CO)_3$ moiety with nearly C_{3v} symmetry, two C(sp^3) atoms from two dimethyl maleate molecules, and the π-bonding C═C group of a cyclobutene ring. Both maleate residues are bonded to adjacent cyclobutene sp^3 carbon atoms by one of their former olefinic maleate carbon atoms and then to Fe through their other olefinic carbon. In terms of the Dewar–Chatt description of metal–alkene bonding, the cyclobutene ring has been twisted by ca. 45° with respect to the Fe dπ-donor orbitals, a consequence of the formation of the two-carbon bridges between the Fe atom and the sp^3 carbon atoms of the ring. Hence the alkene π^*-acceptor orbitals are unable to achieve as strong an interaction as usual with the π orbitals of Fe. This is reflected by the long Fe—(C═C) π bond (mean Fe–C distance 2.26 (2) Å) and by the observed C═C bond length of 1.35 (1) Å, a value which is virtually that of a normal alkene bond. Full-matrix least-squares refinement has converged with a weighted R index (on $|F|$) of 0.051 for the 2779 reflections with $I_o > 2.0\sigma(I_o)$.

Introduction

The utility in organic synthesis of molecules containing metal carbonyl groups coordinated to unsaturated organic moieties has been amply demonstrated.[1] In a continuing effort to characterize molecular cyclobutadiene (C_4H_4) and to extend the synthetic usefulness of this extremely reactive entity, Pettit and coworkers[2-4] have carried out a variety of reactions with $C_4H_4Fe(CO)_3$—an unsaturated iron carbonyl complex which may be considered as a stabilized source of cyclobutadiene for subsequent synthetic use. Thus it has been shown that $C_4H_4Fe(CO)_3$ adds to cycloheptatriene to form I[5] and to the ethylene ketal of tropone to give a complex which upon subsequent degradation (i.e., loss of $Fe(CO)_3$) yields II.[6] If $C_4H_4Fe(CO)_3$ is treated with dimethyl maleate or dimethyl



I



II

Table I. Experimental Summary

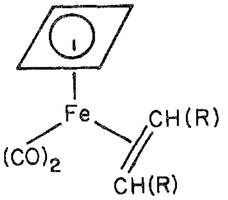
Crystal Data for $C_{16}H_{20}O_8Fe(CO)_3$ (IV)

Formula weight 480.21	Orthorhombic
$a = 15.646$ (2) Å	Systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$
$b = 23.941$ (2) Å	
$c = 11.033$ (1) Å	
$V = 4132.7$ (7) Å^3	Space group $P2_12_12_1$ (No. 19).
$d_{\text{calcd}} = 1.550$ g cm^{-3}	$Z = 8$; $F(000) = 1984$ e
$d_{\text{measd}} = 1.551$ g cm^{-3} (flotation, aqueous $ZnCl_2$)	λ_{Cu}: K$\bar{\alpha}$, 1.54178; Kα_1, 1.54050; Kα_2, 1.54433 Å

Data Collection

Principal crystal faces: 4 faces of {100}, {010}; planes $(00\bar{1})$, (021), $(0\bar{2}1)$
Dimensions: 0.25 × 0.08 × 0.51 mm parallel to a, b, c
$\mu = 8.16$ cm^{-1}
Transmission factors: 0.83–0.94
Syntex $P2_1$ autodiffractometer, graphite-monochromatized Mo Kα radiation, λ_{Mo}(K$\bar{\alpha}$) 0.71069 Å
4064 symmetry-independent reflections for $4° \leq 2\theta \leq 50°$

fumarate, the analogous addition products III are obtained.[4]



$R = CO_2CH_3$

III

Decomposition of III then affords the dicarbomethoxybicyclohexene species, free of metal carbonyl components.

Preparation of cyclobutadieneiron dicarbonyl–dimethyl maleate gave, in addition to the 1:1 adduct III, an appreciable quantity of an unknown yellow solid IV.[7] Subsequent elemental analysis indicated the stoichiometry $C_{19}H_{20}O_{11}Fe$, but the ir and NMR spectra of this material did not allow an unequivocal assignment of a molecular structure. In order to learn the structure of an apparently novel $C_4H_4Fe(CO)_3$ adduct (and thereby to further the understanding of the chemical reactivity of (bound) cyclobutadiene), a single-crystal X-ray diffraction study of this compound was undertaken. Reported herein are the results of that investigation. A preliminary report of the structure of $C_{19}H_{20}O_{11}Fe$ has appeared.[8] An account of the synthesis and chemical behavior of this compound is available elsewhere.[7,9]

Experimental Section

Crystals of IV formed as pale yellow plates from Skelly B solution.[10] Preliminary Weissenberg photographs and plots of the intensity-weighted reciprocal lattice indicated orthorhombic symmetry and systematic absences consistent with space group $P2_12_12_1$. The lattice parameters at 23 (1)°, determined by the least-squares refinement of the 2θ angles of the resolved Cu Kα_1–Kα_2 peaks of 30 intense reflections ($67 < 2\theta < 88°$) carefully centered on a manual General Electric XRD-5 diffractometer (takeoff angle 2°, receiving slit width 0.05°), are presented with other crystal data in Table I.

Intensity data were collected by the ω-scan technique (see Table I) at rates varying from 1.5 to 4.0° min^{-1}, such that more time was devoted to less intense reflections. Each peak was scanned symmetrically over a range of 1.0° through the calculated K$\alpha_{1,2}$ position. Background intensities on each side of the peak were counted for a time equal to half the peak scan time, in positions offset by +1.0 and −1.0° in ω.

During data collection the intensities of four reflections in diverse regions of reciprocal space were reexamined periodically as a check on crystal and instrument stability. An analysis of the 45 sets of these observations according to a method reported previously[11] indicated only random fluctuation in these check reflections during the 95 hr of data collection. Since all correction factors were calculated to be less than ca. 1.5σ, no decay correction was applied to the data.

Standard deviations were assigned to the intensities in accordance with the expression $\sigma(I) = [S^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$ where S is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = S[CT - (B_1 + B_2)]$. The empirical parameter p[12] was assigned a value of 0 during the early refinement and changed to 0.02 during the later stages. The net intensities I were corrected for Lorentz and polarization effects (including those due to reflection of the incident beam by the monochromator) and for absorption.[13] Only the 2779 reflections with $I > 2.0\sigma(I)$ were used in the subsequent calculations which led to the solution and refinement of the crystal structure.

Solution and Refinement of the Structure

For eight molecules per unit cell (see Table I), there must be two formula units of $C_{16}H_{20}O_8Fe(CO)_3$ per asymmetric unit of $P2_12_12_1$. A sharpened Patterson map revealed that the two independent iron atoms per asymmetric unit are separated by ca. 10 Å (eliminating the possibility of a dimeric structure) and that their z coordinates are near $\pm^1/_4$. Hence the ensuing electron density map phased only with the Fe positions possessed false mirrors at $z = \pm^1/_4$, such that each light atom peak also appeared as a false mirror image. Several Fourier maps were computed with the two Fe positions and a few additional atoms located at apparently reasonable sites (viz., Fe—C≡O moieties) well removed from the false mirror. No appreciable portions of this moderately large unknown structure (i.e., 62 nonhydrogen atoms per asymmetric unit) could be identified from these maps. However, as reported by Hodgkin et al.,[14] often when a bias between a pair of pseudosymmetrically related peaks exists, the larger one may correspond to the correct atomic position. Thus by cautious selection of several such peaks adequate differentiation between peaks of subsequent Fourier maps was indeed achieved, and by means of a series of parallel observed and difference Fourier maps, in conjunction with occasional least-squares refinement of atomic positions, all nonhydrogen atoms were gradually located.

Isotropic refinement of this model by full-matrix least-squares methods approached convergence at $R = \sum\|F_o| - |F_c\|/\sum|F_o| = 0.090$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.121$. The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weights w are $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Fe, O, C,[15] and H[16] were used, and the real and imaginary corrections due to anomalous dispersion were applied to the Fe atom scattering function.[17] Least-squares refinement incorporating anisotropic thermal parameters for all atoms was then conducted until convergence was attained, with $R = 0.070$ and $R_w = 0.095$.

At this point the sign of the imaginary component ($\Delta f''$) of the anomalous scattering correction of iron was reversed prior to an additional cycle of refinement to determine whether the correct enantiomorph had been selected. The error indices R and R_w decreased significantly to 0.066 and 0.089, respectively, implying that the appropriate isomer had now been chosen. Moreover, agreement between the geometries of equivalent parts of the structure (especially those of the independent cyclobutene rings) improved in this last cycle of refinement (i.e., the one in which $\Delta f''$ had the opposite sign). Hence the atomic parameters and molecular geometry presented herein are those of the latter isomer.

A difference Fourier at this juncture revealed several peaks (0.4–0.5 e Å^{-3}) which could be attributed to hydrogen atoms. However, of these only the positional parameters of the eight cyclobutene hydrogens refined satisfactorily. The idealized X-ray positions of the remaining eight nonmethyl hydrogen atoms (C–H = 0.95 Å[18]) were then computed for inclusion in the structure factor calculations of the final cycles of refinement. No attempt was made to account for methyl hydrogen atoms which were poorly defined on this difference map. Continued least-squares refinement, now incorporating a value of 0.02 for p in the $\sigma(I)$ expression, resulted in convergence with $R = 0.061$, $R_w = 0.051$, and a standard deviation of an observation of unit weight, $[\sum w(\|F_o| - |F_c\|)^2/(m - s)]^{1/2}$, of 1.61, where m (2779) is the number of observations ($|F_o|$) and s (583) is the number of variables in least-squares refinement. When all 4064 symmetry-independent data examined in this work are used to calculate structure factors, $R = 0.099$ and $R_w = 0.054$.[19]

To carry out anisotropic refinement of this structure the independent variables had to be divided into three (structurally related) blocks. In order to allow for possible effects of parameter correlation between

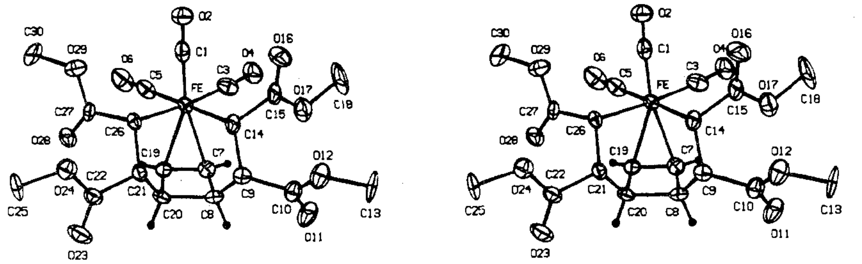


Figure 1. A stereoview of molecule A, illustrating the atom-numbering scheme employed for both independent molecules of the structure. Ellipsoids of 30% probability are shown. Cyclobutene ring hydrogen atoms are drawn as spheres of radius 0.5 Å.

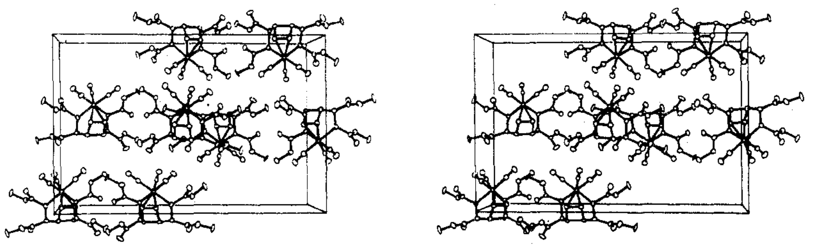


Figure 2. A stereoview of the unit cell. Ellipsoids of 20% probability are shown.

pseudosymmetrically related atoms (vide infra), each block included corresponding atoms from both molecules of the asymmetric unit. Thus the parameters describing the two iron atoms together with their immediate coordination environments constituted one block, and the remaining parameters were divided between two other blocks, so that each block contained about 235 variables. To achieve some parameter overlap during refinement, some parameters were included in more than one block.

In the final cycle of least-squares refinement all shifts in nonhydrogen positional parameters were less than 10% of a corresponding estimated standard deviation (esd), except those for the *y* (12%) and *z* (16%) coordinates of atoms O(3B) and O(24A), respectively. No shift in an anisotropic thermal parameter exceeded 21% of its esd in this final cycle. All shifts in ring hydrogen positional parameters were less than 10% of their esd's. Hydrogen thermal parameters were not refined.

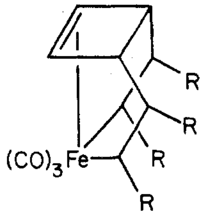
A final difference Fourier synthesis showed several peaks with densities 0.3–0.5 e Å^{-3} scattered about the unit cell. Some of these peaks apparently corresponded to methyl hydrogen atoms, but most of these were too far from established portions of the structure to be significant. From Figure 2 it is clear that the thermal motions of the methyl groups are large, and hence the contributions of their hydrogen atoms to the measured intensities are undoubtedly quite small.

Independent molecules A and B are related by a pseudo-*b*-glide plane (vide infra). Although correlation between pseudosymmetrically related atomic parameters may be troublesome[20] in least-squares refinement, no high correlation between variables was noted during the course of this refinement; no correlation coefficient exceeded 0.5.

Discussion

Figure 1 presents a stereoview of molecule A and indicates the atom numbering sequence used for both molecules A and B. Figure 2 is a stereoview of the contents of the unit cell. Final fractional coordinates and thermal parameters with corresponding standard deviations as estimated from the inverse matrix are listed in Table II. Bond lengths and bond angles are given in Tables III and IV.

The crystal structure is composed of discrete molecules of $C_{16}H_{20}O_8Fe(CO)_3$—the closest nonbonded approach between nonhydrogen atoms is 2.86 (1) Å. (A tabulation of nonbonded distances is available.[19]) Two symmetry-independent molecules are related by a pseudo-*b*-glide parallel to the crystallographic *bc* plane, at $x \simeq 0.26$. Thus, the eight molecules per unit cell are arranged approximately as eight equivalent molecules would be in the centrosymmetric space group *Pbca*.



R = CO_2CH_3
IV

Each Fe atom of IV is coordinated by an irregular octahedron of carbon atoms consisting of a nearly planar array of two cis CO ligands and two σ-bonding sp^3 carbon atoms—one from each of two dimethyl maleate molecules which have added to the cyclobutene ring—and with the third CO ligand and the midpoint of the π-bonding C=C portion of the cyclobutene group occupying the remaining trans vertices. The bond angles about atoms Fe(A) and Fe(B) (exclusive of those involving the alkene carbons C(7) and C(19)) are close to 90° (81.9 (4)–92.9 (4)°), and the dihedral angles between the least-squares planes described by atoms Fe, C(3), C(5), C(14), C(26) and Fe, C(1), C(7), C(19) (see Figure 1) are 91.5 and 90.7° for molecules A and B, respectively.

The $Fe(CO)_3$ fragments exhibit near-C_{3v} symmetry with characteristic bond distances and angles (e.g., mean Fe—C = 1.805 (15) Å, mean C≡O = 1.14 (1) Å).[21] The four Fe–C(sp^3)σ bonds (two/independent molecule) average 2.143 (16) Å, in agreement with values reported for other similar bonds: in dibenzosemibullvaleneiron, Fe–C = 2.141 and 2.137 Å (esd's not given);[22] in $(CO)_2Fe(\pi\text{-}C_5H_4CH_2)Fe(CO_4)$, Fe–C = 2.123 (15) Å;[23]; in 1,5-cyclooctadienebis(iron tetracarbonyl), Fe–C = 2.154 (4) and 2.140 (6) Å.[24] However, the iron–alkene π bonds in IV (mean Fe–C(alkene) = 2.265 (21) Å) appear to be ca. 0.1 Å longer than those usually determined. For example, in the parent cyclobutadiene species the observed iron to ring carbon bond lengths are 2.05 (1) to 2.06 (1) Å,[25] in $C_{12}H_8Fe(CO)_4$ the Fe–C(alkene) distances are 2.156 (4) and 2.146 (3) Å,[26] in $(CN)C_2H_3Fe(CO)_4$ the two Fe–C (alkene) distances average 2.10 (1) Å,[27] and in the cluster compound $As(CH_3)_2Fe_3(CO)_9$, in which the Fe atoms are coordinated in an approximately octahedral manner, the Fe to π-bonded carbon distances are 2.05 (2) and 2.20 (2) Å.[28] Consistent with the long Fe to C=C distances in IV are the

Table II a. Fractional Atomic Coordinates and Anisotropic Thermal Parameters (×10^4) for $C_{16}H_{20}O_8Fe(CO)_3$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(A)[b]	−0.11542 (7)	−0.13662 (5)	−0.24106 (13)	279 (5)	112 (2)	581 (12)	12 (3)	33 (9)	21 (6)
C(1A)	−0.1891 (7)	−0.1264 (4)	−0.3622 (10)	42 (6)	10 (2)	91 (12)	−2 (3)	12 (7)	−1 (5)
O(2A)	−0.2352 (4)	−0.1174 (3)	−0.4389 (7)	40 (4)	22 (2)	101 (8)	1 (2)	−17 (5)	3 (4)
C(3A)	−0.1728 (7)	−0.0885 (5)	−0.1425 (10)	41 (6)	22 (3)	70 (1)	4 (3)	0 (7)	14 (5)
O(4A)	−0.2134 (5)	−0.0584 (3)	−0.0850 (7)	54 (4)	24 (2)	108 (9)	10 (2)	17 (5)	−13 (4)
C(5A)	−0.1762 (7)	−0.1935 (5)	−0.1774 (10)	38 (6)	17 (3)	97 (13)	6 (3)	14 (7)	10 (5)
O(6A)	−0.2142 (5)	−0.2297 (3)	−0.1390 (8)	54 (4)	21 (2)	181 (12)	3 (2)	32 (6)	24 (4)
C(7A)	−0.0118 (6)	−0.1260 (4)	−0.1018 (9)	42 (6)	17 (3)	54 (10)	3 (3)	−4 (6)	−3 (4)
C(8A)	0.0644 (6)	−0.1111 (4)	−0.1811 (9)	21 (4)	18 (2)	62 (10)	−1 (3)	−6 (5)	0 (4)
C(9A)	0.0497 (6)	−0.0679 (4)	−0.2789 (8)	28 (4)	16 (2)	54 (11)	0 (3)	7 (5)	1 (4)
C(10A)	0.0790 (6)	−0.0095 (4)	−0.2335 (10)	41 (5)	15 (2)	78 (11)	−5 (3)	12 (7)	−2 (5)
O(11A)	0.1047 (5)	0.0006 (3)	−0.1339 (7)	79 (5)	22 (2)	81 (7)	−12 (3)	−27 (5)	−6 (3)
O(12A)	0.0747 (5)	0.0275 (3)	−0.3228 (7)	66 (5)	18 (2)	79 (8)	−9 (2)	2 (5)	1 (3)
C(13A)	0.0958 (8)	0.0857 (4)	−0.2875 (10)	96 (8)	8 (2)	134 (15)	−18 (3)	4 (9)	−11 (4)
C(14A)	−0.0420 (6)	−0.0717 (4)	−0.3278 (9)	44 (5)	10 (2)	67 (10)	−4 (3)	0 (6)	5 (4)
C(15A)	−0.0941 (7)	−0.0183 (4)	−0.3237 (12)	45 (6)	8 (2)	136 (15)	−6 (3)	5 (9)	10 (5)
O(16A)	−0.1428 (5)	−0.0044 (3)	−0.4026 (9)	61 (5)	20 (2)	209 (14)	1 (3)	−45 (7)	26 (4)
O(17A)	−0.0868 (4)	0.0093 (3)	−0.2154 (7)	55 (4)	16 (1)	154 (10)	1 (2)	24 (5)	−7 (3)
C(18A)	−0.1426 (9)	0.0587 (5)	−0.2108 (14)	105 (9)	14 (3)	268 (26)	21 (4)	39 (13)	−13 (7)
C(19A)	−0.0131 (7)	−0.1800 (4)	−0.1331 (10)	39 (6)	13 (2)	60 (11)	1 (3)	−16 (6)	1 (4)
C(20A)	0.0624 (6)	−0.1744 (4)	−0.2201 (10)	23 (5)	15 (2)	64 (12)	6 (2)	−7 (6)	1 (4)
C(21A)	0.0422 (6)	−0.1869 (4)	−0.3525 (9)	30 (5)	9 (2)	74 (11)	2 (3)	4 (6)	1 (4)
C(22A)	0.0891 (5)	−0.2381 (4)	−0.3985 (9)	25 (4)	14 (2)	97 (10)	4 (3)	6 (6)	3 (4)
O(23A)	0.1472 (5)	−0.2619 (3)	−0.3492 (7)	42 (4)	33 (2)	140 (10)	21 (3)	−13 (6)	−20 (4)
O(24A)	0.0580 (4)	−0.2552 (3)	−0.5051 (7)	45 (4)	18 (2)	83 (7)	1 (2)	−2 (5)	−3 (3)
C(25A)	0.0954 (7)	−0.3051 (4)	−0.5619 (11)	75 (7)	10 (2)	160 (15)	12 (3)	0 (10)	−20 (5)
C(26A)	−0.0563 (6)	−0.1895 (4)	−0.3704 (8)	32 (5)	10 (2)	55 (9)	3 (3)	4 (5)	−4 (4)
C(27A)	−0.0897 (6)	−0.2473 (4)	−0.3580 (9)	31 (5)	9 (2)	75 (11)	−4 (3)	15 (6)	−11 (4)
O(28A)	−0.0585 (4)	−0.2841 (3)	−0.2958 (6)	46 (4)	11 (1)	114 (9)	3 (2)	−4 (4)	10 (3)
O(29A)	−0.1616 (4)	−0.2544 (3)	−0.4215 (7)	39 (4)	23 (2)	128 (9)	−2 (2)	−27 (5)	0 (4)
C(30A)	−0.2015 (7)	−0.3095 (4)	−0.4177 (13)	55 (7)	12 (2)	230 (21)	−22 (3)	−31 (10)	4 (6)
Fe(B)[b]	−0.40425 (7)	−0.50889 (5)	−0.24697 (14)	335 (6)	130 (3)	558 (12)	−4 (3)	−47 (10)	13 (6)
C(1B)	−0.3347 (7)	−0.4938 (4)	−0.3715 (11)	40 (6)	12 (2)	96 (13)	4 (3)	−12 (7)	0 (5)
O(2B)	−0.2935 (5)	−0.4862 (4)	−0.4536 (8)	53 (4)	24 (2)	122 (10)	−1 (2)	27 (6)	3 (4)
C(3B)	−0.3542 (6)	−0.4572 (4)	−0.1502 (9)	43 (5)	19 (2)	71 (10)	0 (3)	−17 (6)	1 (4)
O(4B)	−0.3170 (5)	−0.4269 (3)	−0.0902 (7)	68 (5)	24 (2)	101 (9)	−14 (3)	−25 (6)	−10 (4)
C(5B)	−0.3301 (7)	−0.5609 (5)	−0.1881 (10)	50 (7)	22 (3)	73 (12)	−6 (3)	−21 (7)	6 (5)
O(6B)	−0.2811 (5)	−0.5917 (3)	−0.1546 (8)	72 (5)	20 (2)	146 (11)	7 (3)	−43 (6)	3 (4)
C(7B)	−0.5086 (6)	−0.5029 (4)	−0.1017 (9)	44 (5)	17 (3)	52 (10)	2 (3)	5 (6)	2 (4)
C(8B)	−0.5869 (6)	−0.4942 (4)	−0.1779 (8)	40 (5)	15 (2)	56 (9)	−4 (3)	12 (6)	−2 (4)
C(9B)	−0.5786 (6)	−0.4503 (4)	−0.2763 (9)	32 (5)	17 (2)	62 (11)	1 (3)	2 (6)	−5 (4)
C(10B)	−0.6157 (6)	−0.3943 (4)	−0.2324 (10)	45 (5)	16 (2)	57 (10)	4 (3)	−10 (7)	1 (5)
O(11B)	−0.6396 (5)	−0.3842 (3)	−0.1329 (6)	66 (5)	19 (2)	69 (7)	8 (2)	16 (5)	−7 (3)
O(12B)	−0.6198 (5)	−0.3576 (3)	−0.3265 (6)	61 (4)	22 (2)	65 (7)	14 (2)	−6 (5)	−3 (3)
C(13B)	−0.6501 (9)	−0.3006 (4)	−0.2925 (10)	126 (10)	12 (2)	123 (15)	24 (4)	−4 (10)	2 (5)
C(14B)	−0.4863 (6)	−0.4480 (4)	−0.3294 (8)	40 (5)	12 (2)	40 (9)	3 (3)	−1 (6)	3 (4)
C(15B)	−0.4425 (6)	−0.3938 (4)	−0.3220 (9)	36 (5)	18 (2)	81 (10)	−3 (3)	7 (6)	13 (4)
O(16B)	−0.3945 (5)	−0.3764 (3)	−0.3980 (7)	59 (4)	18 (2)	106 (8)	−4 (2)	20 (5)	13 (3)
O(17B)	−0.4561 (4)	−0.3670 (3)	−0.2171 (6)	51 (4)	17 (2)	95 (9)	0 (2)	5 (4)	−8 (3)
C(18B)	−0.4125 (8)	−0.3118 (4)	−0.2017 (11)	92 (8)	11 (2)	150 (16)	−18 (4)	−6 (10)	−10 (5)
C(19B)	−0.5003 (7)	−0.5576 (4)	−0.1346 (9)	44 (6)	16 (3)	50 (10)	2 (4)	2 (6)	1 (4)
C(20B)	−0.5770 (6)	−0.5568 (4)	−0.2176 (8)	25 (4)	16 (2)	62 (11)	−3 (2)	5 (5)	3 (4)
C(21B)	−0.5573 (6)	−0.5684 (4)	−0.3509 (9)	37 (5)	11 (2)	69 (10)	2 (3)	3 (6)	6 (4)
C(22B)	−0.5975 (7)	−0.6231 (4)	−0.3948 (10)	30 (5)	19 (3)	86 (12)	4 (3)	−8 (7)	−2 (5)
O(23B)	−0.6498 (4)	−0.6503 (3)	−0.3400 (6)	42 (3)	24 (2)	119 (8)	−9 (2)	7 (5)	−5 (3)
O(24B)	−0.5705 (4)	−0.6355 (3)	−0.5052 (6)	50 (4)	19 (2)	84 (8)	−3 (2)	−2 (5)	−12 (3)
C(25B)	−0.6109 (8)	−0.6839 (4)	−0.5593 (11)	92 (8)	16 (2)	110 (13)	−6 (4)	0 (10)	−22 (5)
C(26B)	−0.4597 (6)	−0.5664 (4)	−0.3739 (8)	25 (5)	13 (2)	60 (9)	−3 (3)	−8 (5)	3 (4)
C(27B)	−0.4197 (6)	−0.6207 (4)	−0.3582 (9)	35 (5)	19 (2)	60 (10)	−7 (3)	−6 (6)	−1 (4)
O(28B)	−0.4455 (4)	−0.6591 (3)	−0.2964 (7)	46 (4)	14 (1)	115 (10)	5 (2)	8 (5)	7 (3)
O(29B)	−0.3441 (4)	−0.6244 (3)	−0.4196 (6)	40 (3)	15 (2)	101 (8)	1 (2)	17 (5)	−4 (3)
C(30B)	−0.2954 (7)	−0.6770 (4)	−0.4057 (12)	52 (6)	15 (2)	180 (17)	9 (3)	14 (9)	−8 (5)

b. Fractional Coordinates and Assigned Isotropic Thermal Parameters (Å^2) for Some Hydrogen Atoms of $C_{16}H_{20}O_8Fe(CO)_3$[c]

Atom	x	y	z	B	Atom	x	y	z	B
H(7A)[d]	−0.034 (5)	−0.103 (3)	−0.041 (7)	3	H(7B)[d]	−0.483 (5)	−0.484 (3)	−0.017 (7)	3
H(8A)	0.112 (5)	−0.102 (3)	−0.134 (7)	3	H(8B)	−0.641 (5)	−0.490 (3)	−0.131 (7)	3
H(19A)	−0.035 (5)	−0.212 (3)	−0.100 (8)	3	H(19B)	−0.476 (5)	−0.590 (3)	−0.091 (8)	3
H(20A)	0.095 (5)	−0.190 (4)	−0.200 (8)	3	H(20B)	−0.626 (5)	−0.580 (3)	−0.177 (7)	3
H(9A)*	0.098	−0.075	−0.336	5	H(9B)*	−0.605	−0.459	−0.350	5
H(14A)*	−0.050	−0.074	−0.420	5	H(14B)*	−0.485	−0.460	−0.422	5
H(21A)*	0.068	−0.152	−0.394	5	H(21B)*	−0.581	−0.534	−0.403	5
H(26A)*	−0.067	−0.177	−0.461	5	H(26B)*	−0.441	−0.548	−0.457	5

[a] See Figure 1 for the atom numbering sequence. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For atoms Fe(A) and Fe(B) the anisotropic thermal parameters are given ×10^5. [c] Numbers in parentheses are the estimated standard deviations in the units of the least significant digits. Coordinates of atoms marked with asterisks represent idealized positions which were not refined. [d] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound.

Table III. Interatomic Distances (A) for $C_{16}H_{20}O_8Fe(CO)_3$[a]

	Molecule A	Molecule B		Molecule A	Molecule B
Fe–C(1)	1.782 (11)	1.790 (11)	O(12)–C(13)	1.48 (1)	1.49 (1)
Fe–C(3)	1.821 (11)	1.813 (9)	C(9)–C(14)	1.54 (1)	1.56 (1)
Fe–C(5)	1.804 (11)	1.821 (12)	C(14)–C(15)	1.52 (1)	1.47 (1)
Fe–C(14)	2.158 (9)	2.145 (9)	C(15)–O(16)	1.20 (2)	1.20 (1)
Fe–C(26)	2.121 (9)	2.147 (9)	C(15)–O(17)	1.37 (1)	1.34 (1)
Fe–C(7)	2.249 (10)	2.293 (10)	O(17)–C(18)	1.47 (1)	1.50 (1)
Fe–C(19)	2.250 (11)	2.270 (11)	C(20)–C(21)	1.52 (1)	1.53 (1)
Fe–C(8)	2.954 (9)	2.979 (10)	C(21)–C(22)	1.52 (1)	1.53 (1)
Fe–C(20)	2.935 (9)	2.954 (10)	C(22)–O(23)	1.20 (1)	1.21 (1)
C(1)–O(2)	1.13 (1)	1.13 (1)	C(22)–O(24)	1.34 (1)	1.32 (1)
C(3)–O(4)	1.15 (1)	1.14 (1)	O(24)–C(25)	1.47 (1)	1.45 (1)
C(5)–O(6)	1.13 (1)	1.13 (1)	C(21)–C(26)	1.56 (1)	1.55 (1)
C(7)–C(8)	1.52 (1)	1.50 (1)	C(26)–C(27)	1.49 (1)	1.46 (1)
C(7)–C(19)	1.34 (2)	1.36 (2)	C(27)–O(28)	1.22 (1)	1.21 (1)
C(19)–C(20)	1.53 (1)	1.51 (1)	C(27)–O(29)	1.34 (1)	1.37 (1)
C(8)–C(20)	1.58 (1)	1.57 (1)	O(29)–C(30)	1.46 (1)	1.48 (1)
C(8)–C(9)	1.51 (1)	1.52 (1)	C(7)–H(7)	0.93 (8)	1.12 (8)
C(9)–C(10)	1.56 (1)	1.54 (1)	C(8)–H(8)	0.94 (8)	1.00 (8)
C(10)–O(11)	1.20 (1)	1.18 (1)	C(19)–H(19)	0.91 (8)	0.99 (8)
C(10)–O(12)	1.33 (1)	1.36 (1)	C(20)–H(20)	0.67 (9)	1.05 (8)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figure 1 for identity of the atoms.

Table IV. Bond Angles (deg) for $C_{16}H_{20}O_8Fe(CO)_3$[a]

	Molecule A	Molecule B		Molecule A	Molecule B
C(1)–Fe–C(3)	92.4 (5)	93.0 (5)	O(11)–C(10)–O(12)	124.5 (9)	124.1 (9)
C(1)–Fe–C(5)	93.1 (5)	91.4 (5)	C(10)–O(12)–C(13)	114.8 (8)	114.4 (7)
C(1)–Fe–C(7)	164.5 (4)	163.1 (4)	Fe–C(14)–C(9)	112.6 (6)	111.8 (6)
C(1)–Fe–C(14)	85.0 (4)	84.3 (4)	Fe–C(14)–C(15)	107.9 (7)	107.3 (6)
C(1)–Fe–C(19)	157.1 (4)	157.8 (4)	Fe–C(14)–H(14)*	110	102
C(1)–Fe–C(26)	81.9 (4)	82.8 (4)	H(14)–C(14)–C(9)*	118	112
C(3)–Fe–C(5)	89.2 (5)	88.9 (5)	H(14)–C(14)–C(15)*	90	106
C(3)–Fe–C(7)	82.9 (4)	81.5 (4)	C(9)–C(14)–C(15)	116.2 (8)	116.2 (7)
C(3)–Fe–C(14)	94.1 (4)	92.5 (4)	C(14)–C(15)–O(16)	123.4 (10)	124.0 (9)
C(3)–Fe–C(19)	109.1 (4)	108.3 (4)	C(14)–C(15)–O(17)	112.9 (9)	113.5 (8)
C(3)–Fe–C(26)	174.2 (4)	175.4 (4)	O(16)–C(15)–O(17)	123.4 (9)	122.3 (9)
C(5)–Fe–C(7)	101.5 (4)	104.3 (4)	C(15)–O(17)–C(18)	111.7 (9)	116.7 (8)
C(5)–Fe–C(14)	176.3 (4)	175.5 (4)	Fe–C(19)–C(7)	72.7 (6)	73.5 (6)
C(5)–Fe–C(19)	79.7 (4)	82.9 (4)	Fe–C(19)–C(20)	100.2 (6)	100.9 (6)
C(5)–Fe–C(26)	92.4 (4)	92.9 (4)	Fe–C(19)–H(19)	109 (5)	114 (5)
C(7)–Fe–C(14)	80.6 (4)	80.1 (3)	H(19)–C(19)–C(7)	135 (5)	132 (5)
C(7)–Fe–C(19)	34.6 (4)	34.8 (4)	H(19)–C(19)–C(20)	128 (5)	127 (5)
C(7)–Fe–C(26)	102.3 (4)	102.0 (4)	C(7)–C(19)–C(20)	93.8 (8)	94.2 (8)
C(14)–Fe–C(19)	100.8 (4)	100.6 (4)	H(20)–C(20)–C(8)	116 (8)	108 (4)
C(14)–Fe–C(26)	84.2 (3)	85.3 (3)	H(20)–C(20)–C(19)	109 (8)	109 (4)
C(19)–Fe–C(26)	76.7 (4)	76.1 (4)	H(20)–C(20)–C(21)	111 (8)	118 (4)
Fe–C(1)–O(2)	176.9 (9)	176.3 (10)	C(8)–C(20)–C(19)	85.9 (7)	85.4 (7)
Fe–C(3)–O(4)	175.8 (10)	174.8 (9)	C(8)–C(20)–C(21)	117.1 (8)	117.5 (8)
Fe–C(5)–O(6)	179.0 (10)	176.6 (10)	C(19)–C(20)–C(21)	115.2 (8)	114.9 (8)
Fe–C(7)–C(8)	101.4 (6)	101.5 (6)	H(21)–C(21)–C(20)*	101	108
Fe–C(7)–C(19)	72.7 (6)	71.7 (6)	H(21)–C(21)–C(22)*	108	110
Fe–C(7)–H(7)	107 (5)	111 (4)	H(21)–C(21)–C(26)*	111	103
H(7)–C(7)–C(8)	125 (5)	135 (4)	C(20)–C(21)–C(22)	112.3 (8)	112.2 (8)
H(7)–C(7)–C(19)	138 (5)	126 (4)	C(20)–C(21)–C(26)	109.6 (8)	110.5 (8)
C(8)–C(7)–C(19)	95.1 (8)	93.6 (8)	C(22)–C(21)–C(26)	113.9 (7)	112.4 (8)
H(8)–C(8)–C(7)	111 (5)	115 (4)	C(21)–C(22)–O(23)	126.6 (9)	125.5 (10)
H(8)–C(8)–C(9)	111 (5)	112 (4)	C(21)–C(22)–O(24)	111.5 (7)	110.6 (8)
H(8)–C(8)–C(20)	113 (5)	109 (4)	O(23)–C(22)–O(24)	121.9 (9)	123.8 (10)
C(7)–C(8)–C(9)	116.8 (8)	115.3 (8)	C(22)–O(24)–C(25)	118.6 (8)	114.8 (8)
C(7)–C(8)–C(20)	85.2 (7)	86.7 (7)	Fe–C(26)–C(21)	108.9 (6)	108.2 (6)
C(9)–C(8)–C(20)	117.4 (8)	117.0 (7)	Fe–C(26)–C(27)	109.9 (6)	108.8 (6)
C(8)–C(9)–H(9)*	103	115	Fe–C(26)–H(26)*	113	101
C(8)–C(9)–C(10)	109.9 (8)	110.3 (8)	H(26)–C(26)–C(21)*	106	115
C(8)–C(9)–C(14)	110.7 (7)	111.9 (7)	H(26)–C(26)–C(27)*	107	111
H(9)–C(9)–C(10)*	98	108	C(21)–C(26)–C(27)	112.0 (7)	112.1 (8)
H(9)–C(9)–C(14)*	118	95	C(26)–C(27)–O(28)	125.8 (8)	126.9 (9)
C(10)–C(9)–C(14)	116.2 (7)	115.9 (8)	C(26)–C(27)–O(29)	111.5 (8)	111.7 (8)
C(9)–C(10)–O(11)	125.2 (9)	126.1 (9)	O(28)–C(27)–O(29)	122.7 (8)	121.3 (8)
C(9)–C(10)–O(12)	110.3 (8)	109.8 (8)	C(27)–O(29)–C(30)	117.4 (8)	116.6 (7)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figure 1 for identity of the atoms. Atom sequences marked with asterisks contain idealized hydrogen positions and hence are not refined values.

lengths of the two alkene bonds, which average 1.35 (1) Å and hence are close to normal C–C double bonds (1.337 (6) Å[29]).

The obvious weakness of the iron–alkene π bond in IV is apparently due to the constraints imposed upon the orientation of the cyclobutene ring by the two-carbon bridges from Fe to the ring (see Figure 1). Thus, the cyclobutene moiety has been so twisted that the plane containing π-bonded atoms Fe, C(7), C(19) roughly bisects the angle between the planes formed

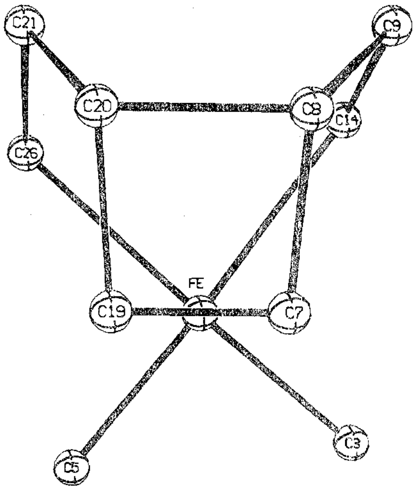


Figure 3. A view of the immediate environment of the Fe atom, showing the orientation of the C(7)–C(19) double bond of cyclobutene with respect to the other atoms of the coordination sphere. Carbonyl atom C(1) is eclipsed by the Fe atom in this projection.

by atoms Fe, C(1), C(3), C(26) and atoms Fe, C(1), C(5), C(14) (see Figure 3). The angle between plane Fe–C(7)–C(19) and plane Fe–C(1)–C(3)–C(26) is 41°, and that between Fe–C(7)–C(19) and plane Fe–C(1)–C(5)–C(14) is 53° in molecules A and B. In a more conventionally coordinated octahedral atom, plane Fe–C(7)–C(19) would be nearly parallel to one of these planes and hence nearly orthogonal to the other. (The angle between planes Fe–C(1)–C(3)–C(26) and Fe–C(1)–C(5)–C(14) is 93° in A and B.)

According to the conventional description of metal–carbonyl bonding[30] the unfilled iron $d_{x^2-y^2}$ and d_{z^2} orbitals (or perhaps dp-hybrid orbitals) form weak σ bonds by accepting electron density from the carbonyl ligands. These preliminary σ bonds are concomitantly reinforced by π bonds formed by "back-donation" of accumulated negative charge on the metal from the filled ("interaxial") $d\pi$ orbitals (viz., d_{xy}, d_{xz}, d_{yz}) to empty π-antibonding (π^*) orbitals of carbon monoxide—a phenomenon commonly referred to as synergic bonding. The alkene residue of the cyclobutene ring bonds with the Fe atom in an analogous synergic manner. Whereas the π^* orbitals of the three carbonyls of this structure are appropriately disposed to overlap effectively with the iron $d\pi$ orbitals, the corresponding π^*-acceptor orbitals of the C=C group have been rotated by ~45° from position of optimum overlap.[31] Hence at best only a minimal metal $d\pi \rightarrow$ alkene π^* interaction seems likely in compound IV. Perhaps what is observed then is the interaction originating solely from the incipient Fe–∥ σ bond (where ∥ is C=C); i.e., in a sense an isolation of the σ portion of a metal–alkene synergic bond.

In accordance with the Dewar–Chatt model of metal–alkene synergic bonding,[30] the decrease in C=C bond order resulting from the flow of electron density from metal to olefin antibonding orbitals may be accompanied by an elongation of the C=C bond. For example, the C=C distances of 1.421 (5) Å found in $C_{12}H_8Fe(CO)_4$[26] and that of 1.401 (9) Å observed in η^2-(*cis*-2,3-dicarbomethoxymethylenecyclopropane)iron tetracarbonyl[32] support this concept. However in IV the mean C=C distance of 1.35 (1) Å suggests little Fe $d\pi \rightarrow$ alkene π^* electron density transfer and is therefore consistent with a weak Fe–∥ π interaction.

The coordinated cyclobutene rings are planar; the dihedral angles between planes C(8)–C(7)–C(19) and C(20)–C(19)–C(7) are 0.9 and 0.8° in molecules A and B, respectively; and no carbon atom of either cyclobutene ring deviates from its four-atom best plane by as much as 1 esd. (A listing of least-squares planes for this structure is available.[19]) As discussed above, the C–C double bond is virtually a normal alkene bond, identical with that found in the cyclobutene ring of bicyclo[4.2.0]-2,4,7-octatrienetricarbonyliron.[33] The four C(sp^2)–C(sp^3) bonds (C(7)–C(8) and C(19)–C(20)) of the two rings average 1.52 (1) Å, equivalent to those observed in 3,4:7,8-dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene.[34] The two C(sp^3)–C(sp^3) bonds (C(8)–C(20)) of the cyclobutenes average 1.58 (1) Å and compare favorably with the corresponding distances given in ref 33 (1.586 Å) and ref 34 (1.593 (7) Å). Finally, the angles around the two rings (exculsive of those involving the unsatisfactorily determined hydrogen positions (C–H range 0.67 (9)–1.12 (8) Å; C–H mean 0.95 (12) Å)) show the same systematic variation as reported earlier.[34]

There are no apparent differences among similar portions of the eight ester moieties. The following average distances (of eight values in this structure) are normal and may be compared to the corresponding bond lengths listed for the ester-containing compound of ref 32: C(sp^3)—C(sp^2) = 1.51 (3) Å, C(sp^2)=O = 1.20 (1) Å, C(sp^2)—O = 1.35 (2) Å, and C(sp^3)—O = 1.48 (2) Å. The apparent lengthening of the last bond (viz., C(sp^3)—O), although probably not significant, can be attributed to the high thermal motion of the methyl groups (see Figure 2) and to the neglect of the contributions of methyl hydrogen atoms to the measured X-ray intensities.

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Supplementary Material Available. Tables of nonbonded interatomic distances for nonhydrogen atoms, least-squares planes and deviations therefrom, and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50264O-10-75.

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Synthesis and Structure of Some Cobalt(II) Complexes with the Tridentate Ligand 1,1,1-Tris(diphenylphospinomethyl)ethane

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The tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, p_3, forms five-coordinate complexes with cobalt(II) with the empirical formula $CoX(p_3)B(C_6H_5)_4$. When X is Cl, Br, or OH, i.e., is a monodentate ligand, the complexes are binuclear with bridging X. The ions $[Co_2X_2(p_3)]^{2+}$ show antiferromagnetic behavior. When X is acetate (ac), nitrate (NO_3), or acetylacetonate (acac), monomeric complexes are formed where magnetic susceptibility obeys the Curie–Weiss law. The hydroxide derivative $[Co_2(OH)_2(p_3)_2][B(C_6H_5)_4]_2 \cdot x(CH_3)_2CO$ crystallizes in the triclinic system, space group $P1$, with unit cell dimensions $a = 16.905\ (3)$ Å, $b = 15.774\ (2)$ Å, $c = 13.850\ (2)$ Å, $\alpha = 111.67\ (3)°$, $\beta = 91.07\ (3)°$, and $\gamma = 115.06\ (4)°$. Each cobalt atom is five-coordinated by three phosphorus atoms from a p_3 ligand and two oxygen atoms from the bridging hydroxide groups. The acetate derivative $[Co(ac)(p_3)][B(C_6H_5)_4] \cdot x(CH_3)_2CO$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 19.995\ (3)$ Å, $b = 19.201\ (3)$ Å, $c = 17.211\ (2)$ Å, and $\beta = 110.44\ (3)°$. The acetate ligand is bidentate and thus the cobalt atom is five-coordinate.

Introduction

The coordinating behavior of the eponymous ligand $CH_3C(CH_2P(C_6H_5)_2)_3$, p_3, toward cobalt ions has been studied in recent years. The reactions fall into three categories.

In the presence of the reducing agent $NaBH_4$, cobalt(II) chloride and bromide are reduced to the tetrahedral cobalt(I) complexes $[CoX(p_3)]$ (X = Cl, Br);[1] the iodide is spontaneously reduced without added reducing agent.[1] Other cobalt(II) salts yield, in the presence of $NaB(C_6H_5)_4$, the triply bridged dimeric cobalt(II) compound $[Co_2H_3(p_3)_2][B(C_6H_5)_4]$.[2]

When no reducing agent is present, the results are often ambiguous. It has been claimed that the only well-characterized complex to be formed is the thiocyanate $[Co(NCS)_2(p_3)]$.[3] The recently prepared complexes $[CoX_2(p_3)]$ (X = Cl, Br)[4] have some physical properties suggestive of the presence of phosphine oxide, while the agreement between observed and calculated analytical figures is based on erroneously calculated values.

In order to clarify the situation we have conducted similar experiments with p_3 and cobalt(II) salts, *with rigorous exclusion of air*; under these conditions well-defined cobalt(II) complexes are obtained. The X-ray crystal structures of the hydroxo and acetato derivatives have helped to clarify the stereochemistry in these systems.

Experimental Section

Reagents. The cobalt salts, sodium tetraphenylborate, ethanol, 1-butanol, acetone, tetrahydrofuran, methylene chloride, and petroleum ether were reagent grade and were used without further purification. The preparation of the ligand has already been described.[5]

Preparation of the Complexes. All operations were performed under dry nitrogen. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

Di-μ-chloro-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate, $[Co_2Cl_2(p_3)_2][B(C_6H_5)_4]_2 \cdot x$(solvent),[6] and Di-μ-bromo-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate, $[Co_2Br_2(p_3)_2][B(C_6H_5)_4]_2 \cdot x$(solvent) (Solvent = Acetone, Methylene Chloride). Anhydrous cobalt(II) halide (1 mmol) in 20 ml of 1-butanol was added, after filtration, to 1 mmol of p_3 and 1 mmol of $NaB(C_6H_5)_4$ in 30 ml of solvent. Red-brown crystals were obtained by evaporation of the dark brown solution. The crystals were washed with butanol and petroleum ether.

Di-μ-hydroxo-bis[1,1,1-tris(diphenylphosphinomethyl)ethane]dicobalt(II) Tetraphenylborate, $[Co_2(OH)_2(p_3)][B(C_6H_5)_4]_2 \cdot x$(solvent) (Solvent = Acetone, THF). $Co(H_2O)_6(BF_4)_2$ or $Co(H_2O)_6(ClO_4)_2$ (1 mmol) in 20 ml of 1-butanol was added to a solution of p_3 (1 mmol) and $NaB(C_6H_5)_4$ (1 mmol) in 15 ml of acetone (or THF). A rapid stream of nitrogen was passed through the mixture to stir it and the color changed slowly to deep brown. After ca. 0.3 hr the red-brown crystals began to separate. They were treated as above.

Acetato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate, $[Co(ac)(p_3)][B(C_6H_5)_4] \cdot x(CH_3)_2CO$, Acetylacetonato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate, $[Co(acac)(p_3)][B(C_6H_5)_4]$, and Nitrato[1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(II) Tetraphenylborate, $[Co(NO_3)(p_3)][B(C_6H_5)_4] \cdot x(CH_3)_2CO$. These compounds which appear as orange-brown crystals were prepared from cobalt(II) acetate, acetylacetonate, and nitrate, respectively, in the same manner as the halide complexes.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recordings of infrared and